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SEMI-ANNUAL PROGRESS REPORT ON THE APPLICATION OF DIFFUSE X-RAY SCATTERING TO THE STUDY OF THE STRUCTURE OF BINARY ALLOYS

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Submitted By
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I. Introductory Comments

The research to be conducted under this grant (NASA Grant NGR-43-001-018) consists of an experimental and theoretical investigation of the relationship between the local atomic arrangements in metallic solid solutions and the physical and mechanical properties of the solid solutions. The local atomic arrangements after varied thermal history are to be investigated using single crystal x-ray diffuse scattering techniques. The results of the diffuse scattering measurements are to be correlated with measurements of physical and mechanical properties, particularly electrical resistivity and hardness.

During the first six months of the grant the bulk of the research effort has been expended toward the growth of satisfactory alloy single crystal specimens for the x-ray diffuse scattering experiments and the development of the necessary experimental apparatus for both x-ray and resistivity measurements. Progress has been made in both of these areas and in addition some x-ray measurements have been performed on Ni-10 at. % W and Ni-20 at. % Mo alloys. The following paragraphs give more detailed discussions of each of these aspects of our research.

II. Growth of Alloy Single Crystals

A number of modifications of the Bridgman technique have been tried in an effort to obtain satisfactory single crystals of the following alloys: Ni-5 at. % W, Ni-10 at. % W, Fe-14.5 at. % Al, Fe-18.7 at. % Al, Fe-22.5 at. % Al, Ag-25 at. % Zn, and Ni-50 at. % Pd. It has been found much easier to grow crystals of certain of these alloys than for others. Fe-Al crystals appear to have a greater propensity for growth than the others listed. To date, we have successfully grown crystals of Ni-10 at. % W, Fe-14.5 at. % Al, and Fe-18.7 at. % Al. The Fe-Al crystals have been prepared from iron of two different starting purities -- a high purity 99.999% Fe and an electrolytic iron of approximately 99.9% purity.

The most successful technique used so far has been to slow cool a melt under inert atmosphere in a temperature gradient established by a tubular silicon carbide heating element. The disadvantages of this technique include 1) the short life of the heating element at operating tem-

eratures in the range 1500° to 1600°C, and 2) the lack of a very sharp gradient. Other techniques tried have included induction melting and moving the induction coil so as to obtain directional solidification. Very sharp temperature gradients are maintained by this technique but problems have been encountered with thermal cracking of crucible materials, principally high purity alumina.

We believe that many of the crystal growth problems encountered thus far can be circumvented by using a noble metal wound resistance furnace capable of operation up to 1750°C in conjunction with a mechanism for moving this furnace vertically as in the standard Bridgman technique. The mechanism for moving such a furnace is presently under construction and available furnaces are being investigated.

III. Development of Experimental Apparatus

The diffuse scattering monochromator. In order to perform diffuse scattering measurements on iron-bearing samples CoKα radiation must be used in order to eliminate the fluorescence which would occur if CuKα radiation were used. It is also necessary to use a doubly-bent crystal monochromator in order to obtain a sufficient intensity of highly monochromatic radiation (1). We have designed and constructed such a monochromator for cobalt radiation. This monochromator has some distinquishing features which will now be described.

The usual diffuse scattering monochromator uses the (200) reflection from a LiF crystal. While the use of LiF gives a high intensity in the diffracted beam, it is necessary to use Ross balanced filters with such monochromators in order to remove the half-wavelength radiation which also passes such monochromators. We have used germanium as the monochromator crystal. The diamond cubic structure of germanium precisely eliminates the half-wavelength radiation and hence makes balanced filters unnecessary. The fact that it is not necessary to take the difference between intensity measurements obtained with two different filters results in improved precision in the measurements and/or a reduction in the total counting time necessary to obtain equivalent precision for a given intensity. It is believed that this factor outweighs the fact that the beam diffracted from germanium is somewhat less intense than that diffracted from LiF.

In order to obtain the appropriate double curvature a special form of germanium known as dendrite "web" germanium was used. This material consists of very thin (approximately 0.006 inch thick) single crystal germanium which solidifies as a web between two germanium dendrites when pulled from the melt. By using slivers of web germanium approximately two centimeters long and one millimeter wide it was possible to approximate the appropriate doubly-curved surface by bending (at room temperature) and gluing the web germanium strips into a form machined from stainless steel. Preliminary investigation has indicated that the CoKα radiation from this germanium monochromator will be quite satisfactory for diffuse scattering measurements. A more complete discussion of this monochromator will be presented in the future.

Single crystal orienter and cryostat. Other special items necessary for x-ray diffuse scattering measurements are a means for orienting the single crystals in the x-ray diffractometer and a means for heating and cooling the samples. After considerable investigation we have purchased a Siemens diffractometer goniometer and Eulerian cradle. This device is capable of orienting the single crystals in the x-ray beam with an accuracy of six minutes of arc. This accuracy is quite sufficient for diffuse scattering measurements.

It has been necessary to design and construct a device for heating and cooling the x-ray samples during the diffuse scattering measurements. The liquid nitrogen cryostat to be used for cooling the sample to 78°K while mounted on the Eulerian cradle is shown as a cross section view in Figure 1. This cryostat incorporates the following features in its design:

1) The sample is clamped against a copper cold finger which dips into liquid nitrogen, thus allowing the sample to reach thermal equilibrium with the boiling liquid nitrogen.
2) A vacuum is maintained between the walls of the double-wall container and throughout the space immediately surrounding the sample. This provides thermal insulation and prevents condensation on the sample surface.
3) An hemispherical beryllium dome surrounds the sample and acts

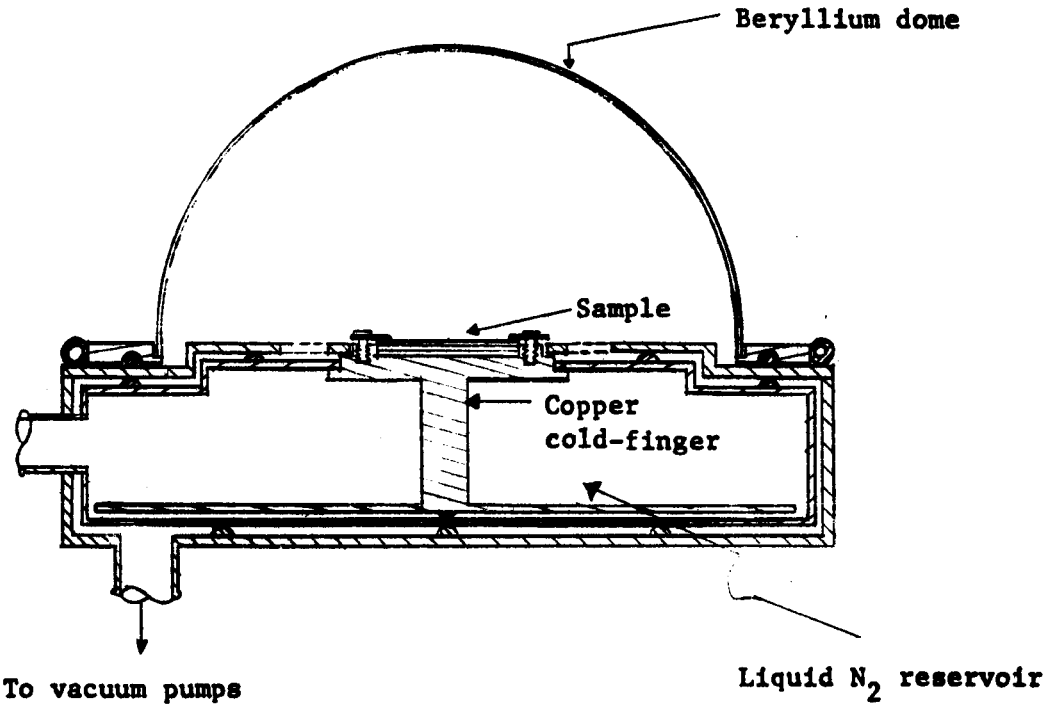

Figure 1. Liquid Nitrogen Cryostat

as both a vacuum seal and x-ray window. This hemispherical shaped window allows measurements to be made throughout a volume in reciprocal space without the necessity of an absorption correction.

When it is desired to heat the sample to high temperatures rather than cool it, the cryostat will be replaced by a similar device which contains a small heater embedded in a copper block behind the sample. The sample will be protected from oxidation by maintaining it in a vacuum. The vacuum seal will again be obtained by the same beryllium dome used on the cryostat.

The cryostat, with the exception of the hemispherical beryllium dome has now been completed-- the dome itself is presently under construction. The design for the device for heating the sample has been completed and construction will begin soon.

The components of the diffuse scattering apparatus are thus nearing completion. Approximately one more month will be required for the integration of these components and the check out procedure before useful data on iron-base alloys can be obtained.

IV. Data Analysis

One aspect of our research which has progressed very satisfactorily is the preparation of computer programs for the analysis of the x-ray data. Fortunately, Fortran programs for many of the analysis techniques which we desire to use were available from the literature or from personal communication with other investigators in the field. A program written by De Angelis (2) has been modified for use in performing the Stokes correction and Fourier analysis of particle size and strain broadening of x-ray line profiles. At present we are beginning to apply this program to the analysis of x-ray data from a Ni-20 at. % Mo single crystal. The object of this study is to correlate the antiphase domain size and strain occurring in this alloy to hardness and resistivity measurements in an effort to determine which factor is more effective in causing the marked hardening observed to accompany the formation of the long range ordered phase in this alloy. The results of this investigation are as yet too scant to report.

Other programs which have been prepared and are beginning to be useful include a program for performing a Fourier analysis of x-ray diffuse scattering determined in a plane in reciprocal space and a program for determining the chemical composition of iron-aluminum alloys by finding the best value of the lattice parameter of the alloy and relating this to the composition through the empirical relation of Taylor and Jones (3). The first of these programs is a modification of one graciously supplied to us by Dr. C. J. Sparks of Oak Ridge National Laboratory.

A program for analyzing diffuse scattering data taken throughout a volume in reciprocal space is presently being developed.

V. Diffuse Scattering Measurements on Ni-10 at. % W

The diffuse scattering in the h_1h_20 plane of reciprocal space for a Ni-10 at. % W alloy quenched in iced brine from 1300°C is presented in Figure 2. No formal analysis of this data has yet been made; nowever, it is interesting to note the great similarity of this data to that obtained from a Ni-10.7 at. % Mo crystal (4). The positions of the diffuse maxima appear in the same positions in the two systems. This indicates that the short-range structure of the Ni-10 at. % W alloy consists of remanents of the structure of the intermetallic compound Ni_4W.

In order to obtain addition information it will be necessary to perform a Fourier analysis of this and additional data. Our goal in this project is to learn how short-range structure affects the physical and mechanical properties of alloys. The data shown in Figure 2 are only a beginning. With this beginning it should be possible for us to make considerable progress toward this goal in the next few months.

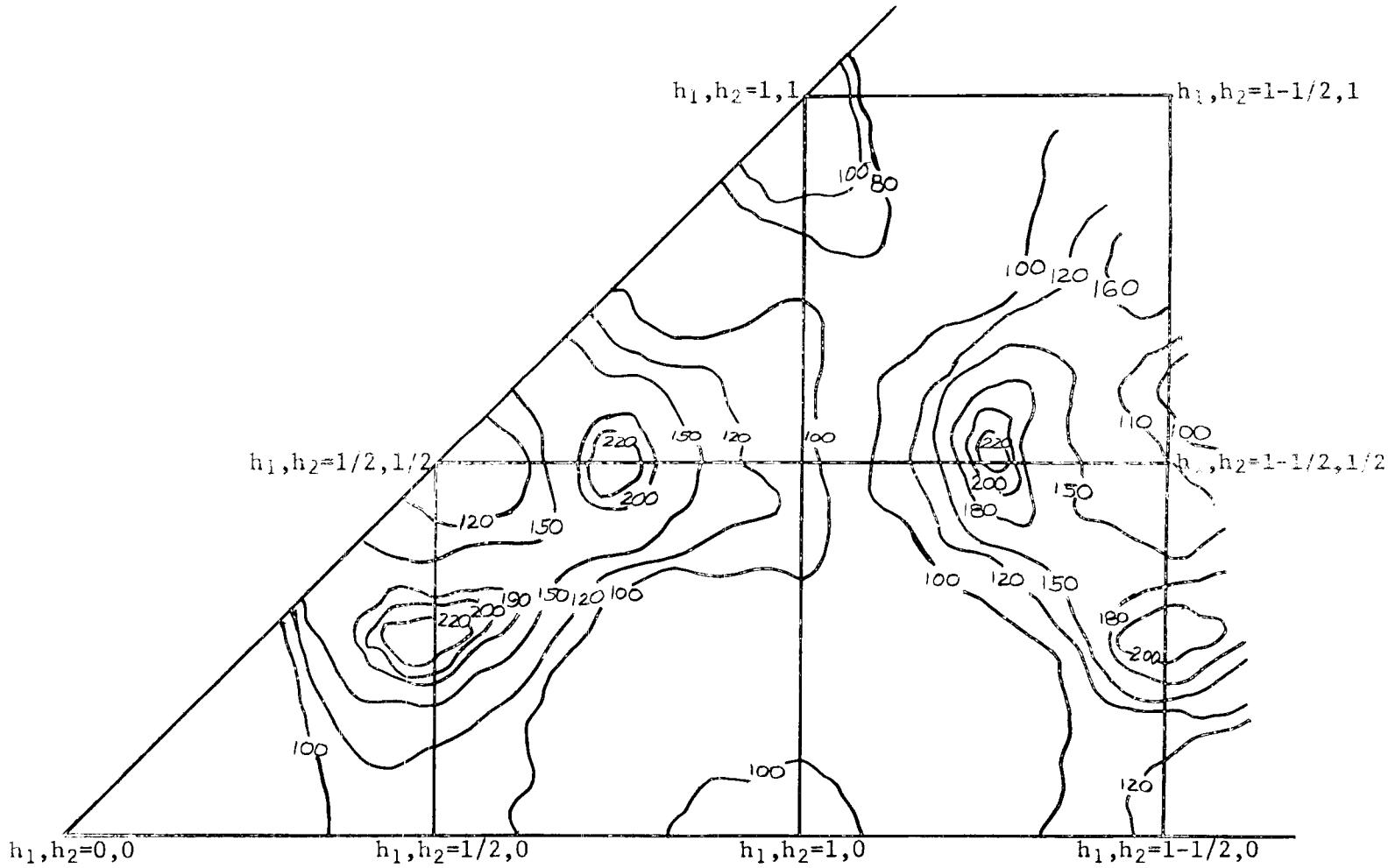

Figure 2. Diffuse intensity distribution in the h_1h_20 plane of reciprocal space for Ni-10 at. % W quenched from 1300°C in iced brine. Data have been corrected for Compton and temperature diffuse scattering. Units are Ieu X $100/NM_AM_B(f_A-f_B)^2$.

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